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Geochemistry of the Earth's Surface meeting, GES-10

## Biology as an agent of chemical and mineralogical change in soil

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### Abstract

Earthworms have a significant impact on the functioning of soils and the processes that occur within them. Here we review our work on the impact of earthworms on soil mineralogy and chemistry, in particular focusing on the contribution of earthworms to mineral weathering and calcium carbonate in soils and the impact that earthworms have on metal mobility at contaminated sites.

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**Keywords:** Earthworms; weathering; calcium carbonate; calcite; metal contamination

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### 1. Introduction

It is well established that earthworms make a significant contribution to a variety of soil processes that give rise to ecosystem services<sup>1</sup>. Their burrowing activity aerates the soil and enhances water drainage, they break down organic

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matter consequently releasing nutrients and also mix the soil. Here we briefly review our work on two additional, less well established impacts that earthworms have: changes to soil mineralogy and contaminant mobility.

## 2. Earthworms and mineral weathering

The primary minerals anorthite, biotite and olivine (obtained commercially, ground and sieved to 63 – 250 micron) and the secondary minerals kaolinite, illite and smectite, together with ground manure were used to make artificial soils in which earthworms which occupy three contrasting ecological niches - *Eisenia veneta* (lives in the litter layer), *Allolobophora chlorotica* (lives in mineral-rich soil) and *Lumbricus terrestris* (lives in semi-permanent vertical burrows) – were cultivated<sup>2,3</sup>. For *E. veneta* and *A. chlorotica*, 3 g of mineral and 7 g of manure were mixed and a single earthworm was added to the mixture. For the *Lumbricus terrestris* experiments individual earthworms were kept in 5 cm diameter, 50 cm long tubes containing 30 g of mineral mixed with 270 g of a quartz-dominated sandy loam. Earthworm-free controls were also run. After 1, 2, 4 and 6 months samples were analysed by X-ray diffraction to test for changes in mineralogy. Reductions in peak intensity and broadening of peaks in X-ray traces for the minerals of interest in samples from earthworm treatments compared with controls was taken as evidence of earthworm-enhanced weathering (Table 1). The least amount of weathering was detected for *L. terrestris*. However, this is most likely due to detection issues. The dilution of the mineral of interest by the sandy loam resulted in the XRD signal being dominated by quartz from the sandy loam so that any changes in the trace from the mineral of interest might not have been detected. The results from *E. veneta* and *A. chlorotica* clearly demonstrated that earthworms can accelerate mineral weathering with the effect being more marked in the primary silicates than the secondary minerals. As with much mineral weathering research the challenge lies in translating these results into a firm understanding of the significance of this impact in field scenarios.

Table 1. A summary showing the month (1, 2, 4 or 6) after which increased weathering relative to earthworm-free controls was detected on the basis of peak intensity reduction and / or peak broadening in XRD traces. ? indicates inconclusive evidence for weathering. X indicates no weathering detected. NT indicates mineral was not tested

Mineral	<i>E. veneta</i>	<i>A. chlorotica</i>	<i>L. terrestris</i>
Olivine	?2	NT	NT
Anorthite	2	1	NT
Biotite	4	1	X
Smectite	1	2	X
Kaolinite	4	NT	NT
Illite	NT	X	X

## 3. Earthworms and calcium carbonate

Many species of earthworm secrete granules of calcium carbonate into the soil with the carbonate most likely being produced to regulate internal pH<sup>4</sup>. The calcium carbonate is primarily calcite but aragonite, vaterite and (surprisingly stable) amorphous calcium carbonate may also be present<sup>5-9</sup>. When we have cultured the earthworm *Lumbricus terrestris* in field-sampled metal-rich soils and metal-amended soils we have also detected the presence of cerrusite (PbCO<sub>3</sub>) and Pb-bearing calcite<sup>7</sup>, Sr-rich carbonate<sup>8</sup> and Zn-bearing calcite<sup>9</sup> in the granules. Using X-ray diffraction and X-ray spectroscopy we have shown that whereas Sr is incorporated into the calcite during formation of the granules<sup>8</sup>, the majority of the Pb adsorbs to the granule outer surface prior to secretion of the granules into the soil with some subsequent solid state diffusion into the granules<sup>7</sup> and the majority of the Zn adsorbs to granules post-secretion<sup>9</sup>. The presence of Pb in the granules appears to favour the formation of small amounts of aragonite whilst no aragonite was detected in granules produced by earthworms cultivated in Sr- and Zn-bearing soil. This may be due to the similar crystal structure of cerrusite and aragonite whereas strontianite (SrCO<sub>3</sub>) and smithsonite (ZnCO<sub>3</sub>) have the calcite structure<sup>9</sup>. Granule secreting earthworms can flourish at metal contaminated sites<sup>10-14</sup>. This makes it tempting to speculate that metal incorporation and adsorption onto granules may act as a detoxification mechanism

for the earthworms and / or impact on metal mobility at contaminated sites (due to incorporation or adsorption of metals into relatively insoluble carbonate phases) this appears unlikely due to rates of granule production.

Granule production rates lie in the range 0 – 4.3 mg calcite earthworm<sup>-1</sup> day<sup>-1</sup> increasing with soil pH<sup>15</sup>, temperature<sup>4</sup> and CO<sub>2</sub><sup>4</sup>. Predicted total mass of granules produced per unit area of land depends on estimates of earthworm density but, for contaminated soils and the concentrations of metals recorded in the granules from our metal-rich soil experiments (up to 1577 mg kg<sup>-1</sup> Pb<sup>7</sup>, 34 200 mg kg<sup>-1</sup> Sr<sup>8</sup> and 164 mg kg<sup>-1</sup> Zn<sup>9</sup>) the mass of metal associated with the calcium carbonate is an insignificant percentage of the total metal in the soil. Similarly, these rates of granule production mean that the granules do not represent a large reservoir of soil C. However, the flux of Ca and trace metals due to granule production may be significant compared to other environmental fluxes (Table 2).

Table 2. Elemental flux rates due to granule production and mineral weathering, plant uptake, deposition and runoff. Granule fluxes are calculated from a production rate of 0.05 – 4.3 mg calcite earthworm<sup>-1</sup> day<sup>-1</sup> (REF<sup>15</sup>) and an earthworm density of 200 individuals m<sup>-2</sup> with 1 in 5 earthworms being granule producing. Granule chemistry (5 ± 1 mg kg<sup>-1</sup> Pb, 345 ± 23 mg kg<sup>-1</sup> Sr, 10 ± 2 mg kg<sup>-1</sup> Zn) is for granules produced in an uncontaminated agricultural soil<sup>5</sup>. Other fluxes are taken almost at random from published literature but give an idea of the order of magnitude of the fluxes.

Elemental flux in mg m <sup>-2</sup> a <sup>-1</sup>	Ca	Pb	Sr	Zn
Granule production	280 – 25000	0.004 – 0.315	0.2 – 21.8	0.007 – 0.63
Mineral weathering	80 – 3000 <sup>A</sup>	?	2.7 <sup>A</sup>	?
Plant uptake	50 – 1500 <sup>A</sup>	3.4 <sup>B</sup>	7.2 <sup>A</sup>	27 <sup>B</sup>
Deposition	200 – 400 <sup>C</sup>	2 – 3 <sup>C</sup>	0.8 <sup>A</sup>	5 – 10 <sup>C</sup>
Catchment runoff	2300 <sup>D</sup>	0.04 – 0.36 <sup>E</sup>	10 <sup>D</sup>	0.96 <sup>F</sup>

A Watmough (2014) Biogeochemistry 118 357-369; B Bergkvist (1987) Wat Air Soil Pollut 33 131-154; C DEFRA monitoring data; D Durand et al (1994) J Hydrol 157 139-156; E Bringmark et al (2013) Wat Air Soil Pollut 224:1502; F Ukonmaanaho et al (2001) Environ Pollut 114 63-75;

The preservation of granules in soils is dependent on the saturation state of the soil solution with respect to calcium carbonate<sup>15</sup>. Under the right conditions granules can survive in soils for many thousands of years<sup>15, 16</sup>. Under these conditions they can constitute a not inconsiderable reservoir of soil Ca<sup>15</sup>. More excitingly, we have shown that the oxygen isotopes in the granules vary systematically with the temperature at which the granules formed and that individual granules can be dated using U/Th dating<sup>16</sup>. This suggests that granules could be used in palaeoclimate reconstructions. At present application of our palaeothermometer requires knowledge of the oxygen isotope composition of the soil solution in which the earthworms were living. This has to be estimated on the basis of latitudinal position. However we are currently investigating the use of clumped isotope analysis of the granules to get around this. Should our clumped isotope work be successful we will have both a working palaeothermometer and a means to use the granule isotope systematics to determine the isotopic composition of the past soil solution.

#### 4. Earthworms and metal mobility

The activity of earthworms in contaminated soils increases metal mobility and uptake in plants<sup>17</sup>. Our research indicates that it is the breakdown of organic matter leading to an increase in dissolved organic carbon, release of organic matter bound metals and a reduction in pH that results in the increased mobility of metals<sup>18-21</sup>. A concern then becomes whether earthworm activity can impact on the efficiency of amendments of organic matter or biochar added to metal-contaminated soil as a remedial treatment. In our experiments this is not the case, most likely due to the amendments buffering or swamping any affect that the earthworms have on the soil<sup>22</sup>. It is also interesting to note that, in the presence of earthworms plant growth increased, despite an increase in metal uptake. This suggests that the release of nutrients was a more important effect of the earthworm activity than the release of contaminants, at least as far as impacts on plant growth are concerned.

## 5. Summary

Earthworms have a significant impact on soil chemistry and mineralogy. Incorporating the effects of soil biology into models of soil function and evolution requires an understanding of the causes of these effects but also an understanding of the distribution and behavior of soil organisms. In recognition of this fact we are currently developing agent based models that allow us to predict the behavior and distribution of earthworms in soils<sup>23</sup>.

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